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Pham, Tuan Anh; Song, Fei; Stöhr, Meike

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ARTICLE TYPE

Supramolecular self-assembly of metal-free naphthalocyanine on Au(111)

Tuan Anh Pham,^a Fei Song^a and Meike Stöhr^{*a}

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The self-assembly of metal-free naphthalocyanine (H₂Nc) on the Au(111) surface is studied under ultrahigh vacuum conditions at room temperature by a combination of scanning tunnelling microscopy (STM), low-energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS). The STM measurements reveal that the molecules form a well-ordered, defect-free structure with a square-like unit cell at monolayer coverage with their molecular plane parallel to the substrate plane. The molecular lattice direction is aligned along one of the principal directions of the underlying Au(111) substrate while the molecular orientation remains unchanged for different domains. XPS measurements show that there is no significant difference in the electronic structure of H₂Nc between monolayer and multilayer coverage. Combining the information obtained from STM, LEED and XPS measurements demonstrates that the self-assembled structure of H₂Nc on Au(111) is mainly stabilized by intermolecular interactions while the molecule–substrate interactions are responsible for the rotational alignment of the molecules with respect to the principal Au directions.

Introduction

Over the past few decades, organic semiconductors have received constantly increasing attention because of their potential applications in organic electronic devices.^{1–3} As organic semiconductors, phthalocyanines (Pcs) and their derivatives have attracted a lot of interest because of the tunability of their chemical, physical and electronic properties by adding specific substituent groups or exchange of the central metal atom.^{4,5} Their outstanding properties make them ideal candidates to be used in various potential applications, e.g. as p-type organic semiconductors in solar and photovoltaic cells, in gas sensing applications, in organic light-emitting diodes or in field-effect transistors.^{6–10}

Currently, the bottom-up self-assembly of organic molecules on solid inorganic surfaces represents a powerful approach for the fabrication of organic thin film-based devices.^{11–13} The successful construction of such molecular devices strongly depends on the possibility to control the final structure together with its properties. The interplay between molecule–molecule and molecule–substrate interactions needs to receive special attention because the influence of the underlying substrate on the molecular arrangements cannot be neglected anymore when only few molecular layers are to be considered. Therefore, the formation and study of surface-supported two-dimensional (2D) self-assembled structures are ideal to investigate this interplay. With respect to 2D layers of Pcs on various substrates, a considerable number of studies have been carried out investigating, among others, the influence of coverage, the role of the central metal atom, and the influence of substituents on both the resulting structure and occurring interactions.^{14–28}

Naphthalocyanines (Ncs) are an important class of Pcs due to their extended delocalized π electron system what is reflected in a modification of their optical and electronic properties in

comparison to simple Pcs.^{29,30} The light harvesting properties of Ncs are superior with respect to Pcs since their light absorption matches better with the solar spectrum what makes them ideal candidates for the usage in optoelectronic devices.^{31–33} However, despite these impressive findings, the number of studies dealing with Ncs adsorbed on surfaces is rather limited. For example, Gopakumar et al. studied the influence of molecular geometry on the 2D island formation from different Ncs on highly oriented pyrolytic graphite.^{34,35} More recently, Mehring et al. reported on the formation of densely packed 2D islands of metal-free naphthalocyanine (H₂Nc) on Au(100).³⁶

Herein, we report on the adsorption behaviour of H₂Nc on Au(111) at monolayer coverage investigated by a combination of scanning tunnelling microscopy (STM), low-energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS). Very recently, Wiggins et al. performed an STM study for H₂Nc on Au(111) focusing mainly on electronic properties investigated by orbital mediated tunnelling spectroscopy,³⁷ while in our study, the prime aim is to examine the delicate interplay between molecule–molecule and molecule–substrate interactions relevant for the formation of 2D self-assembled adlayers of H₂Nc on Au(111) at room temperature. A detailed analysis of STM, LEED and XPS measurements unambiguously demonstrates that the Au substrate has a weak but not negligible influence on the molecular self-assembly. We conclude that the underlying substrate determines the adsorption orientation of the molecules while the intermolecular interactions are responsible for the 2D adlayer formation.

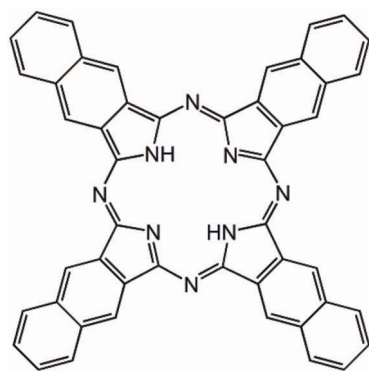
Experimental methods

The experiments were carried out in a two chamber ultrahigh vacuum system with a base pressure of 5×10^{-10} mbar. This

system houses a variable temperature STM (Oxford Instruments Omicron NanoScience), a LEED apparatus (SPECS Surface Nano Analysis GmbH) and an XPS analyser (Thermo Scientific). The Au(111) single crystal was prepared by repeated cycles of sputtering with Ar⁺ ions and annealing at approximately 400 °C. Commercially available 2,3-naphthalocyanine (Sigma-Aldrich, purity 95%) was thoroughly degassed several hours before deposition onto Au(111). The molecules were thermally evaporated from a glass crucible that was heated inside a home-built evaporator. The deposition rate was monitored using a quartz crystal microbalance in order to determine the molecular coverage. The substrate was held at room temperature during deposition. All STM images were taken at room temperature in constant current mode using a platinum-iridium tip. Image processing was done with the free software WSxM.³⁸ The XPS spectra were recorded with a hemispherical energy analyser employing Al K α radiation with a photon energy of 1468.6 eV. The Au 4f_{7/2} core level was used for calibration. LEED pattern simulation was done with LEEDpat.³⁹

Results and discussion

Scheme 1 shows the chemical structure of the H₂Nc molecule which is a planar aromatic macrocycle consisting of a phthalocyanine skeleton with an additional benzene ring attached to each of the four benzopyrrole units. Because only two out of the four nitrogen atoms in the molecular centre bind to hydrogen atoms, H₂Nc has a two-fold symmetry in comparison to a four-fold symmetry found for metal naphthalocyanines. Fig. 1a shows a large-scale STM image after deposition of a monolayer of H₂Nc on the Au(111) substrate. The H₂Nc molecules form a well-ordered two dimensional, defect-free pattern. The herringbone reconstruction of the Au(111) surface is clearly visible through the molecular overlayer. This indicates that the Au reconstruction is neither modified nor lifted upon deposition



Scheme 1. Schematic molecular structure of metal-free naphthalocyanine (H₂Nc)

of H₂Nc. It should be noted that the intact herringbone reconstruction can be regarded as an indication for a weak interaction between the adsorbed molecules and the underlying Au(111) substrate.⁴⁰ The [11 $\bar{2}$] substrate direction is identified via the soliton walls of the surface reconstruction as illustrated by a black arrow in Fig. 1b while the molecular lattice direction is marked by a blue arrow. It turns out that the symmetry axis of

individual H₂Nc molecules is aligned along the [11 $\bar{2}$] direction of the Au(111) substrate. The angle, β , between the molecular lattice direction and the [11 $\bar{2}$] substrate direction is found to be $(30^\circ \pm 3^\circ)$. This means that the molecular lattice direction is parallel to the [1 $\bar{1}$ 0] direction of the underlying Au(111) substrate. Moreover, it is apparent that both the molecular orientation and the molecular adsorption direction remain unchanged across the elbow sites of the herringbone reconstruction. This is in contrast to the findings for H₂Pc on Au(111) from Nilson et al.¹⁹ They assign their observation that the molecular orientation changes at the elbow sites to a dominating molecule–substrate interaction. Besides, for monolayer coverage of CuPc on Au(111), Chizhov et al. found that the molecular rows running along the [1 $\bar{1}$ 0] direction undergo a lateral shift near the elbow sites of the Au(111) herringbone reconstruction due to a change in rotational orientation of individual CuPc molecules.²¹ In our case, however, no such shift of the molecular adsorption direction running along the [1 $\bar{1}$ 0] direction was observed. The reason for these differences might be related to the longer arms of H₂Nc (a naphthalene instead of a benzene unit for Pcs) which enable an interdigitation of the molecules and thereby, more van der Waals interactions between neighbouring molecules. These findings indicate that intermolecular interactions are more significant for the 2D layer formation of H₂Nc on Au(111) compared to the cases of H₂Pc as well as CuPc on Au(111).

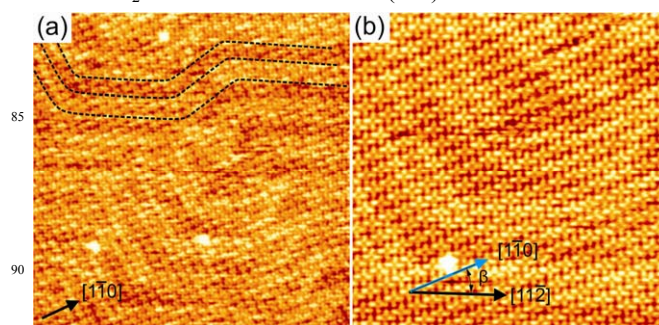


Fig. 1 (a) Overview STM image (50x50 nm²) and (b) a close-up STM image (30x30 nm²) for 1 ML H₂Nc coverage on Au(111). The molecules assemble in a close packed structure (image parameters: U = -1.47 V, I = 40 pA). The herringbone reconstruction of the Au(111) substrate is visible through the molecular layer as indicated by dashed black lines in a). The [11 $\bar{2}$] substrate direction and the molecular lattice direction are denoted by black and blue arrows in b), respectively. The angle, β , formed by these directions is marked in b).

The large-scale STM image in Fig. 2a shows the co-existence of two different domains (labelled A and B) of H₂Nc on Au(111) with the domain boundary marked by a dashed black line. The STM image in Fig. 2b shows the orientation of individual H₂Nc molecules located at the domain boundary in more detail. The molecules in both domains have one of their symmetry axes aligned along the [1 $\bar{1}$ 0] direction of the Au(111) substrate. This indicates that the molecular orientation within both domains is the same with respect to the underlying substrate and thus, the role of the Au substrate in the formation of 2D self-assembled structures from H₂Nc cannot be neglected. One direction of the molecular unit cell of both the A and B domain is parallel to a principal Au direction. However, the unit cells are rotated with respect to each other. That means that the arrangement of the

molecules within the unit cell must differ. In the A domain adjacent molecules are attached to the right side when considering the naphthalene units while in the B domain adjacent molecules are attached to the left side. That means that A and B domain are mirror images of each other with a principal Au direction as mirror plane (blue dotted line in Fig. 2b).

From the high-resolution STM image shown in Fig. 3a, we conclude that the molecules are adsorbed with their molecular plane parallel to the substrate surface. Each H₂Nc molecule is imaged as a symmetric cross-like structure with a depression in the molecular centre which is in good agreement with its chemical structure depicted in Scheme 1. It should be noted that the depression in the centre of H₂Nc observed in STM images can be ascribed to the lack of d-orbitals near the Fermi energy.⁴¹ From the STM analysis, the mean values of the square-like unit cell are found to be $a \approx b = (16 \pm 0.5) \text{ \AA}$ with an internal angle of $(90^\circ \pm 3^\circ)$. The azimuth angle, α , defined as the smallest angle between the molecular axis and a unit cell vector, is determined to be $(30^\circ \pm 3^\circ)$. The azimuth angle is considered as an important parameter in determining the packing density of the molecular overlayer.³⁴ The correlation between the molecular packing density and the azimuth angle can be explained by the competition between repulsive and attractive intermolecular interactions. If the azimuth angle is large, there is less steric repulsion between adjacent molecular lobes (the naphthalene units) resulting in the formation of a close-packed molecular structure. Conversely, if the molecular lobes are close to each

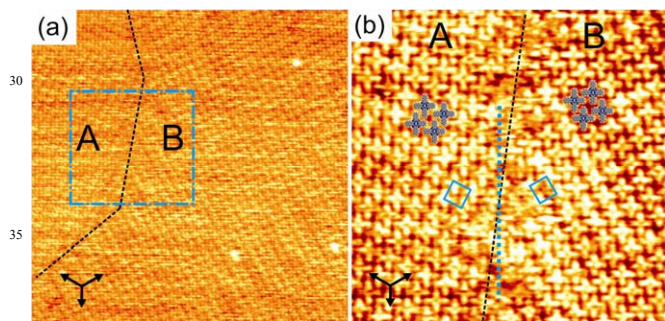


Fig. 2 (a) Overview STM image ($60 \times 60 \text{ nm}^2$, $U = -1.47 \text{ V}$, $I = 40 \text{ pA}$) for 1 ML H₂Nc showing the co-existence of two domains, labelled A and B. (b) Close-up STM image ($30 \times 30 \text{ nm}^2$, $U = -1.47 \text{ V}$, $I = 40 \text{ pA}$) of the area marked by a blue dotted square in (a). For each of the domains, four molecules are drawn in and the unit cells are indicated in blue. The orientation of the molecules with respect to the underlying Au substrate is the same for domain A and B. However, the arrangement of the molecules within the unit cell is mirrored along the blue dotted line, which is parallel to a principal Au direction. The domain boundary is marked by the black dashed lines in (a) and (b). The set of three arrows indicates the principal directions of the underlying Au(111) substrate.

other, steric repulsion between the H atoms of the naphthalene units emerges. As a result, the intermolecular distances increase while the packing density decreases. In the case of dominating intermolecular interactions, the formation of a close-packed 2D overlayer with higher azimuthal angle will occur. In our case, an average molecular density of approximately 0.39 molecules per nm^2 and an azimuth angle of $(30^\circ \pm 3^\circ)$ confirm a close-packed self-assembled structure of H₂Nc molecules on Au(111) what can be regarded as a sign for a weak interaction with the underlying substrate.

In order to precisely determine the molecular unit cell parameters, also with respect to the underlying Au substrate, LEED measurements were performed. Fig. 3b shows a LEED pattern taken at an electron energy of 24 eV for monolayer coverage of H₂Nc on Au(111). For the simulation of the LEED data, the values obtained from the STM analysis were used as starting values. The simulated LEED pattern (Fig. 3c) matches the experimental data quite well. From the simulated LEED pattern, the molecular unit cell dimensions are determined to be $a = b = 16.5 \text{ \AA}$ with an internal angle of 90° while one of the unit cell directions is parallel to the $[1\bar{1}0]$ Au direction. However, the molecular superstructure is incommensurate with the underlying Au substrate. Notably, the existence of an incommensurate superstructure on Au(111) can be considered as evidence for dominating intermolecular interactions.⁴² The LEED data suggest the existence of three domains (marked by different colours in Fig. 3c). In STM we observed three rotational domains

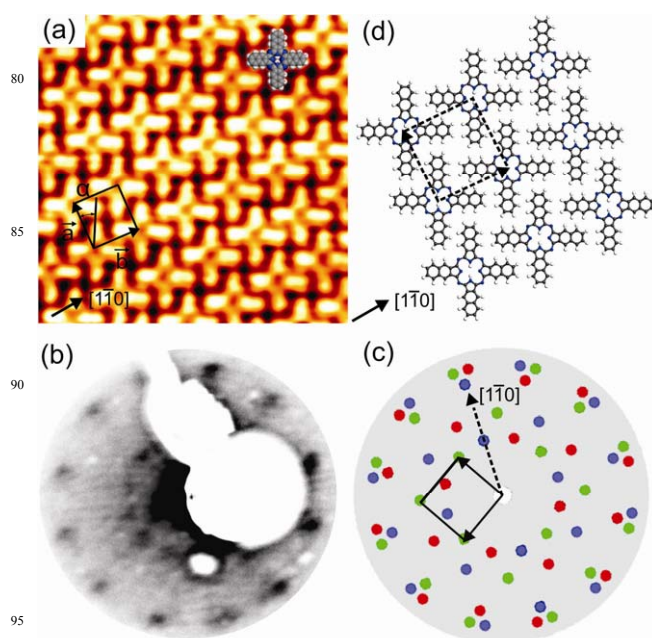


Fig. 3 (a) STM image ($10 \times 10 \text{ nm}^2$, $U = -1.47 \text{ V}$, $I = 40 \text{ pA}$) of 1 ML H₂Nc on Au(111). The molecular unit cell is indicated by a black square with corresponding vectors \vec{a} and \vec{b} . The angle, α , between the molecular axis and the unit cell vector \vec{a} is marked in the figure. (b) Experimentally obtained LEED pattern of 1 ML of H₂Nc on Au(111) taken at a beam energy of 24 eV. (c) Simulated LEED pattern. The different colours mark the rotationally equivalent domains. The black square in (c) indicates the molecular unit cell for one of these domains of the molecular adlayer while the dotted black arrow in (c) shows the $[1\bar{1}0]$ direction of Au(111). (d) Tentative model for the molecular arrangement of H₂Nc on Au(111), the unit cell vectors are denoted by dashed black arrows. Black arrows at the bottom left corner in (a) and (d) indicate the close-packed $[1\bar{1}0]$ direction of the Au(111) substrate.

having an angle of 120° . Considering the existence of mirror domains observed in STM, one would expect the total amount of domains to be six. However, since the unit cell of a mirror domain is equal to the unit cell of a rotational domain (the mirror plane runs along a principal Au direction) the total amount of domains reduces to three. The tentative model for the molecular arrangement based on the information obtained from STM and LEED is depicted in Fig. 3d. Each molecule interacts with four

neighbouring molecules through the naphthalene units which are antiparallel to each other. In this way, van der Waals interactions are established through the interdigitation of the naphthalene units. We assume that these van der Waals interactions are responsible for the development of the observed 2D pattern.

In order to obtain complementary information on the interplay of molecule–molecule and molecule–substrate interactions, XPS measurements of the C1s and N1s core levels were performed for coverages of 1 monolayer (ML) and 2.5 ML. The results are summarized in Table 1. First, we discuss the spectra for monolayer coverage. The C1s core level spectra (Fig. 4, left panel) exhibit two main components corresponding to the two chemically non-equivalent carbon atoms in the molecule. The high intensity peak at a binding energy of 284.2 eV is assigned to the aromatic carbon atoms of the phenyl rings while the weak intensity peak at a binding energy of 286.2 eV is assigned to pyrrolic carbon atoms. The N1s core level spectra show two main components (Fig. 4, right panel). The most intense peak at a binding energy of 398.4 eV is assigned to iminic nitrogen atoms while the weak intensity peak at 400.1 eV is associated with pyrrolic nitrogen atoms. The ratio of the C1s peak intensities amounts to approximately 1:5 (pyrrolic : aromatic carbon) while that of the N1s peak intensities is found to be approximately of 1:3 (pyrrolic : iminic nitrogen), for both 1 ML and 2.5 ML coverages. These results are in good agreement with the stoichiometry of the H₂Nc molecule. Since the top layers for a

LEED and XPS measurements all yield a weak molecule–substrate interaction what means that the structure formation of the self-assembled H₂Nc monolayer on Au(111) is mainly governed by intermolecular interactions.

Table 1 Fitting parameters for 1 ML and 2.5 ML XPS spectra of H₂Nc molecules deposited on Au(111) cf. Fig. 4, uncertainty: 0.1 eV.

Components	1 ML (eV)	2.5 ML (eV)
C 1s (benzene)	284.2	284.2
C 1s (pyrrolic)	286.2	286.2
N 1s (iminic)	398.4	398.4
N 1s (pyrrolic)	400.1	400.1

Conclusions

The adsorption behaviour of H₂Nc on Au(111) was investigated by a combination of STM, LEED and XPS measurements. For monolayer coverage, the molecules form a close-packed, well-ordered 2D structure with a square-like unit cell with the molecular lattice direction parallel to a principal direction of the underlying Au substrate. XPS measurements show that the electronic structure of H₂Nc is hardly influenced by the interaction with the Au substrate. That is concluded by comparing XPS measurements for 1 ML and 2.5 ML. Taken together, these findings unambiguously demonstrate that H₂Nc interacts weakly with the Au substrate and therefore, dominating intermolecular interactions are the main driving force for the self-assembly of H₂Nc on Au(111) at room temperature. Notably, the observation of three and not multiple rotational domains means that the molecules have a preferred adsorption orientation and that the Au substrate has a weak but not negligible role in the molecular self-assembly process. Our study is expected to contribute important information about the interplay of intermolecular and molecule–substrate interactions in the self-assembly of large non-functionalized organic adsorbates on metal substrates in general.

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- ^a Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG, Groningen, The Netherlands. E-mail: m.a.stohr@rug.nl
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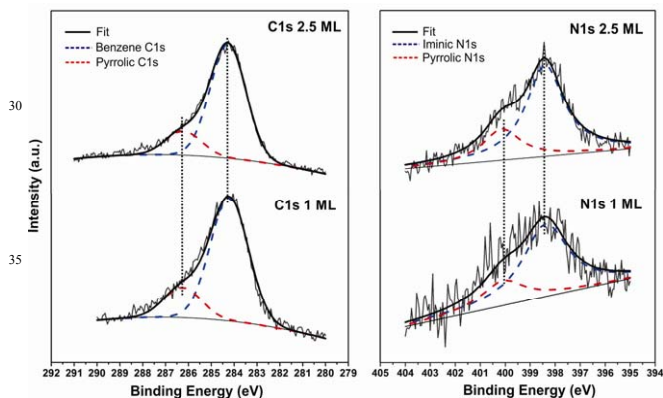


Fig. 4 C1s (left) and N1s XPS spectra (right) of H₂Nc molecules on Au(111) at coverages of 1 ML (lower spectra) and 2.5 ML (upper spectra). The C1s spectra are fitted with two components which can be assigned to the benzene carbon atoms in the phenyl rings (blue dashed line) and the pyrrole carbon atoms in the porphyrazine ring (red dashed line), respectively. The N1s spectra are also fitted with two components. The peak at lower binding energy can be assigned to iminic nitrogen atoms (blue dashed line) while the peak at higher binding energy relates to the pyrrolic nitrogen atoms (red dashed line). The perpendicular black dashed lines indicate that there are no differences in the binding energies of the C1s and N1s core-levels between 1 ML and 2.5 ML coverages.

coverage of 2.5 ML are not in direct contact with the underlying substrate, the change in binding energy for the C1s and N1s components for the two coverages can be used to obtain information on the strength of the molecule–substrate interaction. A careful comparison of 1 ML and 2.5 ML spectra shows that there is no significant shift in binding energy of the C1s and N1s core level energies. These results suggest that the H₂Nc molecules are weakly physisorbed. The findings from STM,

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